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(21) International Application Number: PCT/US99/23255 (22) International Filing Date: 5 October 1999 (05.10.99) (30) Priority Data: 09/168,772 8 October 1998 (08.10.98) US (71) Applicant (for all designated States except US): SYMYX TECHNOLOGIES [US/US]; 3100 Central Expressway, Santa Clara, CA 95051 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): GURAM, Anil, S. [IN/US]; 19930-D Olivewood Street, Cupertino, CA 95014 (US). LaPOINTE, Anne, Marie [US/US]; Apartment 283, 2250 Monroe Street, Santa Clara, CA 95050 (US). TURNER, Howard, W. [US/US]; 2948 Massih Court, Campbell, CA 95008 (US). UNO, Tetsuo [JP/US]; 480 Warren Drive #530, San Francisco, CA 94131 (US). (74) Agents: BELL, Catherine, L. et al.; Frohwitter, Three Riverway, Suite 500, Houston, TX 77056 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CATALYST LIGANDS, CATALYTIC METAL COMPLEXES AND PROCESSES USING SAME		
(57) Abstract New ligands having a backbone comprised of NCCX can be combined with a metal or metal precursor compound or formed into a metal-ligand complex to catalyze a number of different chemical transformations, including polymerization.		

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5 **CATALYST LIGANDS, CATALYTIC METAL COMPLEXES AND
 PROCESSES USING SAME**

FIELD OF THE INVENTION

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 The present invention relates to new organic compounds (e.g., ligands), their metal complexes and compositions using those compounds; the invention also relates to the field of catalysis. In particular, this invention relates to new compounds which when combined with suitable metals or metal precursor compounds provide useful
15 catalysts for various bond-forming reactions, including polymerization, oligomerization or small molecule catalysis. This invention also relates to a method of making the ligands of this invention where the synthesis involves an aryl amination reaction. The invention also relates to combinatorial chemistry in that combinatorial techniques were used in connection with creating the ligands and testing compositions
20 containing the ligands.

BACKGROUND OF THE INVENTION

 Ancillary (or spectator) ligand-metal coordination complexes (e.g.,
25 organometallic complexes) and compositions are useful as catalysts, additives, stoichiometric reagents, monomers, solid state precursors, therapeutic reagents and drugs. Ancillary ligand-metal coordination complexes of this type can be prepared by combining an ancillary ligand with a suitable metal compound or metal precursor in a suitable solvent at a suitable temperature. The ancillary ligand contains functional
30 groups that bind to the metal center(s), remain associated with the metal center(s), and therefore provide an opportunity to modify the steric, electronic and chemical properties of the active metal center(s) of the complex.

 Certain known ancillary ligand-metal complexes and compositions are catalysts for reactions such as oxidation, reduction, hydrogenation, hydrosilylation,
35 hydrocyanation, hydroformylation, polymerization, carbonylation, isomerization, metathesis, carbon-hydrogen activation, carbon-halogen activation, cross-coupling,

Friedel-Crafts acylation and alkylation, hydration, dimerization, trimerization, oligomerization, Diels-Alder reactions and other transformations.

One example of the use of these types of ancillary ligand-metal complexes and compositions is in the field of single site polymerization or oligomerization catalysis.

5 In connection with single site catalysis, the ancillary ligand offers opportunities to modify the electronic and/or steric environment surrounding an active metal center. This allows the ancillary ligand to create possibly different polymers or oligomers. It also allows for higher reactivity under changing process conditions.

Moreover, it is always a desire to discover new ancillary ligands, which upon
10 coordination to a metal center or addition of a metal compound or precursor will catalyze or assist in catalysis of reactions differently from known ligand systems. This invention provides new ancillary ligands that may be used for coordination to a metal center or included in a composition with a metal or metal precursor compound. Upon coordination to the metal center or inclusion in the composition, such ligands
15 influence the electronic and steric environment of the resulting coordination complex and may catalyze reactions differently, including more efficiently and selectively than known systems.

SUMMARY OF THE INVENTION

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In one aspect, the invention disclosed herein is a new ligand, which can be characterized by the general formula:

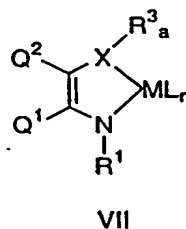
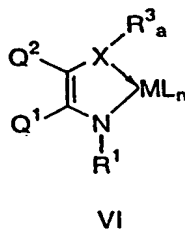
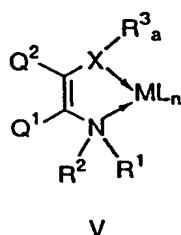


wherein each R^1 , R^2 and R^3 is independently selected from the group consisting of
25 hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, R^1 and R^2 are joined together in a ring structure;
 Q^1 and Q^2 are, independently, selected from the group consisting of hydrogen,
30 alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl,

substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, Q^1 and Q^2 are joined together in a ring structure;

X is selected from the group consisting of O, P, S, and N atoms; and a is 1 or 2, depending on X and its oxidation state.

The ligands can be included in a composition including a suitable metal or metal precursor compound, where the composition has catalytic properties. Also, the ligands can be coordinated with a metal precursor to form metal-ligand complexes, which may be catalysts. The metal-ligand complexes of this invention may be characterized by one of the following the general formulas:



wherein R^1 , R^2 , R^3 , Q^1 , Q^2 , and X are as defined above. In addition, M is a transition metal selected from the group consisting of Groups 4-12 of the Periodic Table of Elements; L is independently each occurrence, a neutral and/or charged ligand; and n is a number 0, 1, 2, 3, 4, and 5, depending on M. If X is nitrogen, a is either 1 or 2 depending on the type of bonding to the metal M. In these formulas, if X is oxygen, then a is either 0 or 1, depending on the type of bonding to the metal M. If X is phosphorus, a is either 1 or 2 depending on the type of bonding to the metal M and the oxidation state of the phosphorus. Similarly, if X is sulfur, a is 0 or 1 depending on the type of bonding to the metal M and the oxidation state of the sulfur.

These transition metal-ligand complexes or compositions catalyze reactions involving activation of and/or formation of H-Si, H-H, H-N, H-O, H-P, H-S, C-H, C-C, C=C, C-C, C-halogen, C-N, C-O, C-S, C-P, and C-Si bonds. Specifically, such reactions include carbonylation, hydroformylation, hydroxycarbonylation, hydrocarbonylation, hydroesterification, hydrogenation, transfer hydrogenation, hydrosilylation, hydroboration, hydroamination, epoxidation, aziridination, reductive amination, C-H activation, insertion, C-H activation-insertion, C-H activation-substitution, C-halogen activation, C-halogen activation-substitution, C-halogen

activation-insertion, cyclopropanation, alkene metathesis, alkyne metathesis, polymerization, alkene oligomerization, alkene polymerization, alkyne oligomerization, alkyne polymerization, co-polymerization, CO-alkene co-oligomerization, CO-alkene co-polymerization, CO-alkyne co-oligomerization and
5 CO-alkyne co-polymerization.

Further aspects of this invention will be evident to those of skill in the art upon review of this specification.

DETAILED DESCRIPTION OF THE INVENTION

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The invention disclosed herein is a new ligand that may be combined with metals or metal precursor compounds to form coordination complexes or compositions of matter, which are useful as catalysts for chemical reactions.

As used herein, the phrase "characterized by the formula" is not intended to be
15 limiting and is used in the same way that "comprising" is commonly used. The term "independently selected" is used herein to indicate that the R groups, e.g., R^1 , R^2 , R^3 , R^4 , and R^5 can be identical or different (e.g. R^1 , R^2 , R^3 , R^4 , and R^5 may all be substituted alkyls or R^1 and R^2 may be a substituted alkyl and R^3 may be an aryl, etc.). A named R group will generally have the structure that is recognized in the art as
20 corresponding to R groups having that name. For the purposes of illustration, representative R groups as enumerated above are defined herein. These definitions are intended to supplement and illustrate, not preclude, the definitions known to those of skill in the art.

The term "alkyl" is used herein to refer to a branched or unbranched, saturated
25 or unsaturated acyclic hydrocarbon radical. Suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), vinyl, n-butyl, t-butyl, i-butyl (or 2-methylpropyl), etc. In particular embodiments, alkyls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

30 "Substituted alkyl" refers to an alkyl as just described in which one or more hydrogen atom to any carbon of the alkyl is replaced by another group such as a halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, and combinations thereof. Suitable substituted alkyls include, for example, benzyl, trifluoromethyl and the like.

The term "heteroalkyl" refers to an alkyl as described above in which one or more hydrogen atoms to any carbon of the alkyl is replaced by a heteroatom selected from the group consisting of N, O, P, B, S, Si, Se and Ge. The bond between the carbon atom and the heteroatom may be saturated or unsaturated. Thus, an alkyl substituted with a heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, or seleno is within the scope of the term heteroalkyl. Suitable heteroalkyls include cyano, benzoyl, 2-pyridyl, 2-furyl and the like.

The term "cycloalkyl" is used herein to refer to a saturated or unsaturated cyclic non-aromatic hydrocarbon radical having a single ring or multiple condensed rings. Suitable cycloalkyl radicals include, for example, cyclopentyl, cyclohexyl, cyclooctenyl, bicyclooctyl, etc. In particular embodiments, cycloalkyls have between 3 and 200 carbon atoms, between 3 and 50 carbon atoms or between 3 and 20 carbon atoms.

"Substituted cycloalkyl" refers to cycloalkyl as just described including in which one or more hydrogen atom to any carbon of the cycloalkyl is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted cycloalkyl radicals include, for example, 4-dimethylaminocyclohexyl, 4,5-dibromocyclohept-4-enyl, and the like.

The term "heterocycloalkyl" is used herein to refer to a cycloalkyl radical as described, but in which one or more or all carbon atoms of the saturated or unsaturated cyclic radical are replaced by a heteroatom such as nitrogen, phosphorous, oxygen, sulfur, silicon, germanium, selenium, or boron. Suitable heterocycloalkyls include, for example, piperazinyl, morpholinyl, tetrahydropyranyl, tetrahydrofuranyl, piperidinyl, pyrrolidinyl, oxazolinyl, and the like.

"Substituted heterocycloalkyl" refers to heterocycloalkyl as just described including in which one or more hydrogen atom to any atom of the heterocycloalkyl is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted heterocycloalkyl radicals include, for example, N-methylpiperazinyl, 3-dimethylaminomorpholine, and

the like.

The term "aryl" is used herein to refer to an aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety.

5 The common linking group may also be a carbonyl as in benzophenone or oxygen as in diphenylether or nitrogen in diphenylamine. The aromatic ring(s) may include phenyl, naphthyl, biphenyl, diphenylether, diphenylamine and benzophenone among others. In particular embodiments, aryls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

10 "Substituted aryl" refers to aryl as just described in which one or more hydrogen atom to any carbon is replaced by one or more functional groups such as alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, alkylhalos (e.g., CF₃), hydroxy, amino, phosphido, alkoxy, amino, thio and both saturated and unsaturated cyclic
15 hydrocarbons which are fused to the aromatic ring(s), linked covalently or linked to a common group such as a methylene or ethylene moiety. The linking group may also be a carbonyl such as in cyclohexyl phenyl ketone.

The term "heteroaryl" as used herein refers to aromatic rings in which one or more carbon atoms of the aromatic ring(s) are replaced by a heteroatom(s) such as
20 nitrogen, oxygen, boron, selenium, phosphorus, silicon or sulfur. Heteroaryl refers to structures that may be a single aromatic ring, multiple aromatic ring(s), or one or more aromatic rings coupled to one or more nonaromatic ring(s). In structures having multiple rings, the rings can be fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group
25 may also be a carbonyl as in phenyl pyridyl ketone. As used herein, rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "heteroaryl."

"Substituted heteroaryl" refers to heteroaryl as just described including in which one or more hydrogen atoms to any atom of the heteroaryl moiety is replaced
30 by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted heteroaryl radicals include, for example, 4-N,N-dimethylaminopyridine.

The term "alkoxy" is used herein to refer to the -OZ¹ radical, where Z¹ is

selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, silyl groups and combinations thereof as described herein. Suitable alkoxy radicals include, for example, methoxy, ethoxy, benzyloxy, t-butoxy, etc. A related term is "aryloxy" where Z^1 is selected from the group consisting of aryl, substituted aryl, heteroaryl, substituted heteroaryl, and combinations thereof. Examples of suitable aryloxy radicals include phenoxy, substituted phenoxy, 2-pyridinoxy, 8-quinolinoxy and the like.

As used herein the term "silyl" refers to the $-SiZ^1Z^2Z^3$ radical, where each of Z^1 , Z^2 , and Z^3 is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.

As used herein the term "boryl" refers to the $-BZ^1Z^2$ group, where each of Z^1 and Z^2 is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.

As used herein, the term "phosphino" refers to the group $-PZ^1Z^2$, where each of Z^1 and Z^2 is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, heteroaryl, silyl, alkoxy, aryloxy, amino and combinations thereof.

The term "amino" is used herein to refer to the group $-NZ^1Z^2$, where each of Z^1 and Z^2 is independently selected from the group consisting of hydrogen; alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

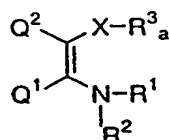
The term "thio" is used herein to refer to the group $-SZ^1$, where Z^1 is selected from the group consisting of hydrogen; alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

The term "seleno" is used herein to refer to the group $-SeZ^1$, where Z^1 is selected from the group consisting of hydrogen; alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl and combinations thereof.

The term “saturated” refers to lack of double and triple bonds between atoms of a radical group such as ethyl, cyclohexyl, pyrrolidinyl, and the like.

The term “unsaturated” refers to the presence one or more double and triple bonds between atoms of a radical group such as vinyl, acetylenyl, oxazoliny,

In one aspect, the ligands of this invention may be characterized by the formula:



10 wherein each R¹, R² and R³ is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, R¹ and R² are joined together in a ring structure;

15 Q¹ and Q² are, independently, selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, Q¹ and Q² are joined together in a ring structure; and

20 X is selected from the group consisting of N, P, S and O atoms; and a is 1 or 2, depending on X.

In more specific embodiments, R¹ and R² are independently selected from a group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, silyl, boryl and phosphino. Specific examples of R¹ and R² are methyl, ethyl, propyl, butyl, cyclohexyl, cyclopropyl, cycloheptyl, t-butyl, phenyl, 2,4,6-trimethylphenyl, 2,4,6-triisopropylphenyl, 2,6-dimethylphenyl, 2,6-diisopropylphenyl, biphenyl, naphthyl, benzyl, pyridyl, furyl, quinolyl, morpholinyl, trimethylsilyl, dimethyl-t-butylsilyl, triphenylsilyl, triethoxysilyl, dimethylboryl, diphenylboryl, diphenoxyboryl, 1,2-dioxyphe-nylboryl, 2,2'-biphenoxyboryl, 2,2'-

dinaphthoxyboryl, diphenylphosphino, dibutylphosphino, dimethylphosphino, dicyclohexylphosphino, dicyclopentylphosphino and methylphenylphosphino. In those embodiments where R^1 and R^2 are joined together in a ring structure, the ring (including R^1 , R^2 , and N) has from 3 to 15 non-hydrogen atoms as part of the backbone of the ring. Specific examples of R^1 and R^2 together are ethylene (giving a 3-membered ring), butylene (giving a 5-membered ring), bicyclooctyl, bicyclohexyl, 2,2'-biphenyl (giving a dibenzo fused 5-membered ring), 2,2'-binaphthyl (giving a dinaphtho fused 5-membered ring) and the like.

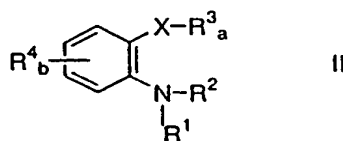
In one preferred embodiment, R^1 is a substituted or unsubstituted phenyl. In the case of the substituted phenyl, there are from 1-5 substituents on the phenyl ring, with each of the substituents independently selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof. Even more preferably, there are 1, 2 or 3 substituents on the substituted phenyl and the substituents are selected from the group consisting of chloro, fluoro, iodo, bromo, methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, phenyl, naphthyl, benzyl, trimethylsilyl and isomers thereof, where applicable. Here and throughout, "where applicable" is intended to mean that for those compounds in the list that have isomers, the isomers are included without having to list each one, which is a form over substance issue. For example, isopropyl, n-butyl, s-butyl, t-butyl are all included isomers.

Also, more specifically, R^3 is selected from a group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl and silyl. Specific examples of R^3 are methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, cyclooctyl, phenyl, naphthyl, benzyl, trimethylsilyl, and the like.

In other embodiments, when X is oxygen or sulfur and a is 1, R^3 is selected from the group consisting of alkyl, substituted alkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl or silyl. In one embodiment, R^3 may be a substituted phenyl having from 1-5 substituents on the phenyl ring, with each of the substituents independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl,

heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof. More specifically, there are typically 1, 2 or 3 substituents on the substituted phenyl and the substituents are selected from the group consisting of chloro, fluoro, iodo, bromo, methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, cyclooctyl, phenyl, naphthyl, benzyl, trimethylsilyl and isomers thereof, where applicable.

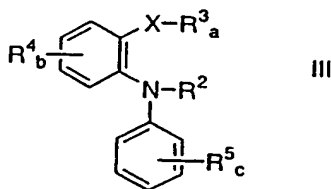
Each of Q^1 and Q^2 is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, boryl, silyl, amino, phosphino, alkoxy, aryloxy, halogens, and combinations thereof. Specific examples of each of Q^1 and Q^2 are methyl, ethyl, propyl, butyl, phenyl, t-butyl, cyclohexyl, benzyl, acetyl, benzoyl, propionyl, pyridyl, morpholinyl, dimethylboryl, dibutylboryl, methylphenylboryl, diphenylboryl, trimethylsilyl, triphenylsilyl, dimethylphenylsilyl, dimethyl-t-butylsilyl, dimethylamino, diethylamino, methylphenylamino, benzylmethylamino, diphenylphosphino, dimethylphosphino, methylphenylphosphino, methoxy, phenoxy, benzyloxy, tetrahydropyranyl, chloro and bromo. Optionally, Q^1 and Q^2 are joined together in a ring structure. In those embodiments where Q^1 and Q^2 are joined together in a ring, the ring (including Q^1 , Q^2 and the two carbon atoms in the backbone of the ligand) has from 4 to 15 non-hydrogen atoms in the backbone of the ring. Specific examples of ring are cyclohexene, cyclopentene, cyclobutene, cyclooctene, cyclopentadiene, naphthalene, anthracene, acridine, dihydrofuran, benzene, pyridine, oxazoline, furan, and thiophene. One form of this option is preferred, such that the ligands of this invention may be characterized by the general formula:



wherein R^1 , R^2 , R^3 , X and a each have the definition given above. In addition, R^4 is selected from the group consisting of electron withdrawing and electron donating groups and b is 0, 1, 2, 3 or 4. More specifically, of R^4 may be chosen from the group

consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, silyl, amino, alkoxy, aryloxy, phosphino, boryl, transition metals, halogens and combinations thereof. Specific examples of R^4 include methyl, ethyl, propyl, butyl, pentyl, hexyl, phenyl, cyano, acetyl, benzoyl, nitro, dimethylamino, diethylamino, methylphenylamino, benzylmethylamino, trimethylsilyl, dimethylboryl, diphenylboryl, methylphenylboryl, dimethoxyboryl, chromium tricarbonyl, ruthenium tricarbonyl, cyclopentadienyl iron, and isomers thereof, where applicable. Optionally, two or more R^4 groups combine to form a fused ring structure with the aromatic group that forms a part of the ligand backbone. The additional fused ring may or may not contain a heteroatom. Examples of the aromatic group that is part of the backbone as combined with two or more R^4 groups that have formed a fused ring are naphthalene, anthracene, quinoline, indole and the like.

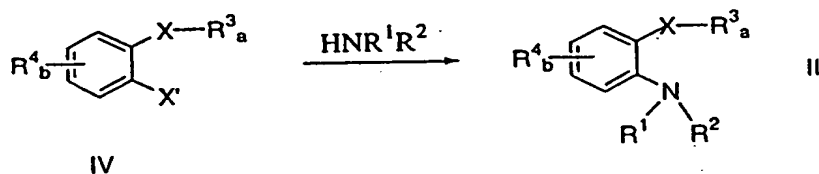
Another embodiment is where the R^1 group is a substituted or unsubstituted phenyl, such that the ligands of this invention may be characterized by the general formula:



- 5 wherein R^2 , R^3 , R^4 , X , a and b each have the definition given above. In addition, R^5 is selected from the group consisting of electron withdrawing and electron donating groups and c is 0, 1, 2, 3, 4 or 5. More specifically, R^5 may be chosen from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, silyl, amino, alkoxy, aryloxy, phosphino, boryl, transition
- 10 metals, halogens and combinations thereof. Specific examples of R^5 include methyl, ethyl, propyl, butyl, pentyl, hexyl, phenyl, cyano, acetyl, benzoyl, nitro, dimethylamino, diethylamino, methylphenylamino, benzylmethylamino, trimethylsilyl, dimethylboryl, diphenylboryl, methylphenylboryl, dimethoxyboryl,
- 15 chromium tricarbonyl, ruthenium tricarbonyl, cyclopentadienyl iron and isomers thereof, where applicable. Optionally, two or more R^5 groups combine to form a fused ring structure with the aromatic group that forms a part of the ligand backbone. The additional fused ring may or may not contain a heteroatom. Examples of the aromatic group that is part of the backbone as combined with two or four R^5 groups
- 20 that have formed a fused ring are naphthalene, quinoline, indole, anthracene and the like, either substituted or not.

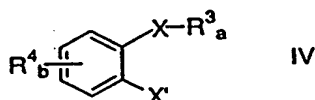
The preferred ligands are synthesized using an aryl amination reaction. The synthesis can be carried out in solution phase or solid phase (using organic or inorganic supports). For solid-phase synthesis, the ligands may be left on the support

25 and used with metal added metal complexes as heterogeneous catalysts. Alternatively, the ligands can be cleaved either before or after reaction with a metal precursor and then used as a homogeneous catalyst. One the general route for synthesis of the ligands of this invention is shown below in scheme 1:



Scheme 1

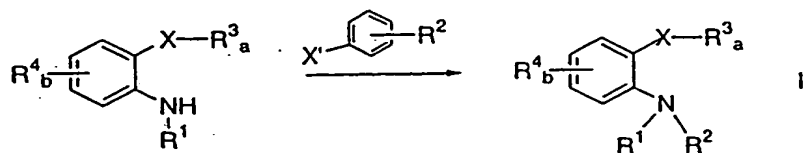
where X' is a leaving group, such as a halogen, like Br, Cl, F or I or an aryl sulfonate, an alkyl sulfonate, triflate, nonaflate or another suitable leaving group. As shown in
 5 scheme 1, the synthesis employs an aryl amination reaction to attach the nitrogen group to the benzene ring at the appropriate location. The aryl amination reaction starts with a compound characterized by the general formula:



wherein R^3 , R^4 , X, a and b are as defined above and X' is selected from the group
 10 consisting of chloro, bromo, iodo, triflate, nonaflate, alkyl sulfonates, aryl sulfonates and tosylate. Starting compounds of this type can be purchased from Aldrich Chemical Company or prepared using known techniques. See, e.g., Greene, Theodora W. and Wuts, Peter G.M., *Protecting Groups in Organic Synthesis*, 2nd Edition (John Wiley & Sons, New York, New York 1991), herein incorporated by reference.

15 The aryl amination reaction uses an amine that can be characterized by the general formula HNR^1R^2 , where R^1 and R^2 are as defined above. This aryl amination reaction is typically performed using a catalyst that comprises known or possibly new metal and ligand catalyst compositions. For example, the catalyst for the aryl amination reaction may be characterized by the general formula M'/L' , where M' is a
 20 complex that contains a metal selected from the group consisting of late transition metals, preferably a Group 10 metal such as Pd, Ni or Pt. M' is any homogeneous or heterogeneous metal precursor catalyst or catalyst. L' is a ligand that may be selected from the group consisting of phosphine or nitrogen ligands. L' may be monodentate, bidentate, tridentate, hemi-labile, unsubstituted or substituted, supported or
 25 unsupported, water-soluble or insoluble, soluble or insoluble in organic solvents including fluorinated solvents. The reaction can take place at known conditions, such as a temperature of from room temperature to about 150°C. Aryl amination reactions are described in U.S. Patent No. 5,576,460, herein incorporated by reference.

In some embodiments, it may be desirable to add a specific R^2 group. In this case, the ligands can be made by starting with R^2 as hydrogen and then adding a reactant to replace the hydrogen with the desired group in a reaction that may be characterized as shown below in Scheme 2:



Scheme 2

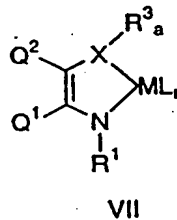
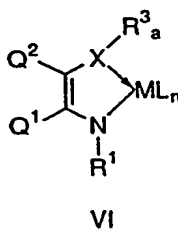
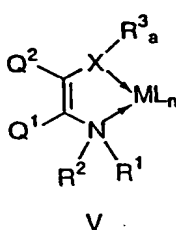
Once the desired ligand is formed, it may be combined with a metal atom, ion, compound or other metal precursor compound. In many applications, the ligands of this invention will be combined with such a metal compound or precursor and the product of such combination is not determined, if a product forms. For example, the ligand may be added to a reaction vessel at the same time as the metal or metal precursor compound along with the reactants. The metal precursor compounds may be characterized by the general formula $M(L)_n$ where M is a metal selected from the group consisting of Groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table of Elements. In more specific embodiments, M is selected from the group consisting of V, Ta, Ti, Zr, Zn, Cr, W, Mo, Ru, Os, Co, Ni, Pd, Fe and Mn. L is a ligand chosen from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, hydrido, thio, seleno, phosphino, amino, and combinations thereof. When L is a charged ligand, L is selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, cyclopentadienyl, substituted cyclopentadienyl, imido, oxo and combinations thereof. When L is a neutral ligand, L is selected from the group consisting of carbon monoxide, isocyanide, nitrous oxide, PA_3 , NA_3 , OA_2 , SA_2 , SeA_2 , and combinations thereof, wherein each A is independently selected from a group consisting of alkyl, substituted alkyl, heteroalkyl,

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cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, and amino. Specific examples of suitable metal precursor compounds include Pd(dba)₂ (dba = dibenzylideneacetone), Pd(OAc)₂ (Ac = acetate) and the like. In this context, the ligand to metal precursor compound ratio is in the range of about 0.01:1 to about 100:1, more preferably in the range of about 0.5:1 to about 20:1.

In other applications, the ligand will be mixed with a suitable metal precursor compound prior to or simultaneous with allowing the mixture to be contacted to the reactants. When the ligand is mixed with the metal precursor compound, a metal-ligand complex may be formed, which may be a catalyst.

In one form, the metal-ligand complexes may be characterized by one of the following general formulas:



wherein each R¹, R², R³, Q¹, Q² and X are as defined above; M is a transition metal selected from the group consisting of Groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table of Elements; L is independently each occurrence, a neutral and/or charged ligand; n is a number 0, 1, 2, 3, 4, and 5, depending on M and L; and a is 0, 1 or 2 depending on the element chosen for X and the type of bonding to M. For example, if X is oxygen or sulfur and the bonding is a dative bond (shown by the arrow), then a is 1. Similarly, if X is oxygen or sulfur and the bonding is a covalent bond, then a is 0. In other embodiments, X will be nitrogen that is datively bonded to M, meaning that a is 2. If X is nitrogen that is covalently bonded to M, then a is 1. In more specific embodiments, M is selected from the group consisting of V, Ta, Ti, Zr, Zn, Cr, W, Mo, Ru, Os, Co, Ni, Pd, Fe and Mn.

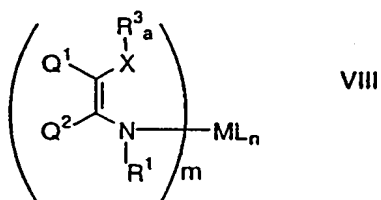
L is independently each occurrence, a neutral and/or charged ligand. Generally, L is a ligand chosen from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy,

aryloxy, hydroxy, boryl, silyl, hydrido, thio, seleno, phosphino, amino, cyclopentadienyl, substituted cyclopentadienyl, imido, oxo and combinations thereof.

When L is a charged ligand, L is selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof. When L is a neutral ligand, L is selected from the group consisting of arene, carbon monoxide, isocyanide, nitrous oxide, PA₃, NA₃, OA₂, SA₂, SeA₂, and combinations thereof, wherein each A is independently selected from a group consisting of alkyl, substituted alkyl, heteroalkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, and amino.

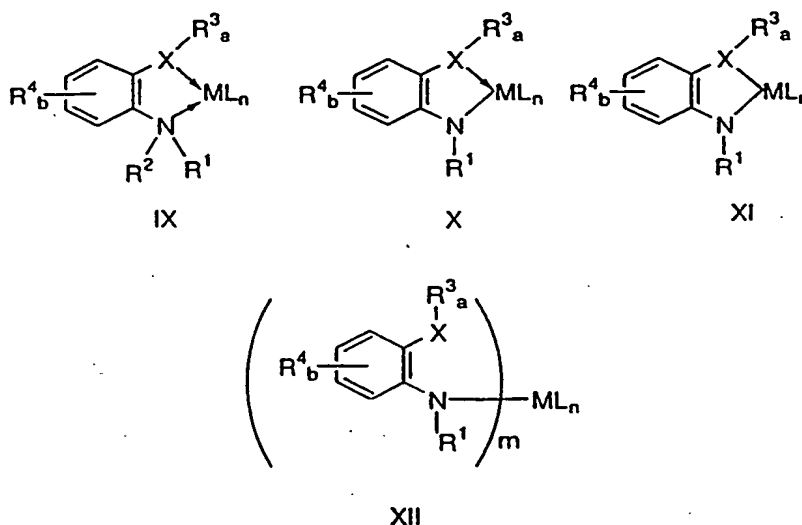
n is the number 0, 1, 2, 3, 4, and 5. M can be neutral, cationic or anionic.

In yet another alternative form, the metal can bind only to the N atom. The various ligand embodiments can be rewritten in this form. For example, the metal complexes may be characterized by one of the general formulas:



where in each R¹, R³, R⁴, Q¹, Q², X, M, L, a, b and n are as defined above; and m is a number that is either 1, 2, 3 or 4.

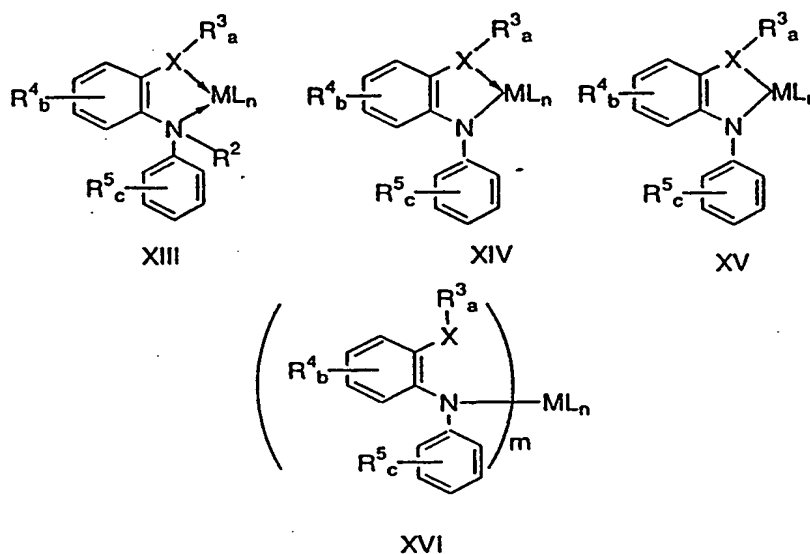
When a preferred form of the ligand is employed, the metal complexes of this invention may be characterized by one of the following the general formulas:



wherein each of R^1 , R^2 , R^3 , R^4 , M , L , X , a , b , m and n are as defined above.

When other preferred ligands are used, the metal complexes may be characterized by one of the following general formulas:

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wherein each of R^2 , R^3 , R^4 , R^5 , M , L , X , a , b , c , m and n are as defined above.

The ligands of this invention bind to a metal via the N and X atoms, optionally via only the N atom, as explained above. Coordination modes described above may
10 or may not depend on the nature of ligands L on the metal M , and for a given

ancillary ligand of this invention the coordination modes may switch from one to another at different stages of a catalytic cycle.

These transition metal-ligand complexes catalyze reactions involving activation of and formation of bonds between H-Si, H-H, H-N, H-O, H-P, H-S, C-H, C-C, C=C, C• C, C-halogen, C-N, C-O, C-S, C-P, and C-Si. Specifically, such reactions include carbonylation, hydroformylation, hydroxycarbonylation, hydrocarbonylation, hydroesterification, hydrogenation, hydrosilylation, hydroboration, hydroamination, epoxidation, aziridination, reductive amination, C-H activation, insertion, C-H activation-insertion, C-H activation-substitution, C-halogen activation, C-halogen activation-substitution, C-halogen activation-insertion, alkene metathesis, alkyne metathesis, polymerization, alkene oligomerization, alkene polymerization, alkyne oligomerization, alkyne polymerization, co-polymerization, CO-alkene co-oligomerization, CO-alkene co-polymerization, CO-alkyne co-oligomerization and CO-alkyne co-polymerization. These reactions may occur at previously known conditions (or possibly novel conditions). Moreover, these reactions may be homogeneous or heterogeneous. In the case of heterogeneous reactions, the ligands may be supported, with or without the metal coordinated, on an organic or inorganic support. Suitable supports include silicas, aluminas, zeolites, polyethyleneglycols, polystyrenes, polyesters, polyamides, peptides and the like.

Polymerization or oligomerization catalysis with the compositions and metal complexes of this invention is a particularly effective process. In particular, the complexes and compositions of this invention are active catalysts also for the polymerization of olefins, possibly in combination with an activator or activating technique. When an activator or activating technique is used, those of skill in the art may use alumoxanes, strong Lewis acids, compatible noninterfering activators and combinations of the foregoing. The foregoing activators have been taught for use with different metal complexes in the following references, which are hereby incorporated by reference in their entirety: U.S. Patents 5,599,761, 5,616,664, 5,453,410, 5,153,157, 5,064,802, and EP-A-277,004. Preferred activators include methylalumoxane, trimethylaluminum, AgBF₄, AgBPh₄, AgBAR'₄, NaBAR'₄, H(OEt₂)₂BAR'₄ and the like (where Ar' is a substituted aromatic, like perfluorophenyl or 3,5-(CF₃)₂(C₆H₃)). An example of a Lewis acid activator is B(C₆F₅)₃.

Ratios of neutral complex to activator are on the order of 1 to 1000 to 1000 to 1. A scavenger can also be used with this invention. Scavengers useful herein

include metal complexes, alumoxanes, aluminum alkyls, Lewis acids and the like. Other additives that are standard for polymerization reactions can be used.

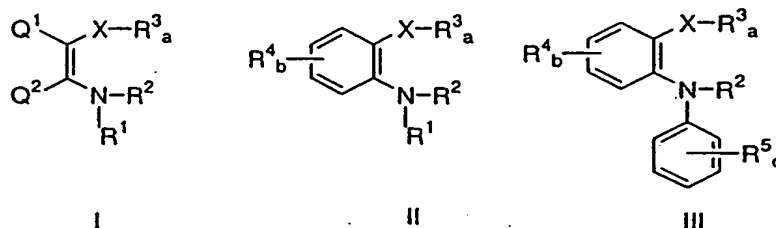
The catalysts herein may be used to polymerize ethylenically or acetylenically unsaturated monomers having from 2 to 20 carbon atoms either alone or in
5 combination. Monomers include C_2 to C_{20} -olefins such as ethylene, propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, styrene and mixtures thereof.

The compounds and catalysts of this invention usefully polymerize functionalized monomers, such as acetates and acrylates. Novel polymers, copolymers or interpolymers may be formed having unique physical and/or melt flow
10 properties. Such novel polymers can be employed alone or with other polymers in a blend to form products that may be molded, cast, extruded or spun. End uses for the polymers made with the catalysts of this invention include films for packaging, trash bags, foams, coatings, insulating devices and household items. Also, such functionalized polymers are useful as solid supports for organometallic or chemical
15 synthesis processes.

Polymerization can be carried out in the Ziegler-Natta or Kaminsky-Sinn methodology, including temperatures of from 0°C to 400°C and pressures from atmospheric to 3000 atmospheres. Suspension, solution, slurry, gas phase or high-pressure polymerization processes may be employed with the catalysts and
20 compounds of this invention. Such processes can be run in a batch or continuous mode. Examples of such processes are well known in the art. A support for the catalyst may be employed, which may be alumina, silica or a polymers support. Methods for the preparation of supported catalysts are known in the art. Slurry, suspension, solution and high-pressure processes use a suitable solvent as known to
25 those skilled in the art.

The ligands, metal-ligand complexes and compositions of this invention can be prepared and tested for catalytic activity in one or more of the above reactions in a combinatorial fashion. Combinatorial chemistry generally involves the parallel or rapid serial synthesis and/or screening or characterization of compounds and
30 compositions of matter. U.S. Patent No. 5,776,359 generally discloses combinatorial methods and WO 98/03521 discloses combinatorial methods for organometallic chemistry, both of which are incorporated herein by reference. In this regard, the ligands, complexes or compositions may be prepared and/or tested in rapid serial and/or parallel fashion, e.g., in an array format. When prepared in an array format,

for example, the ligands may be take the form of an array comprising a plurality of compounds wherein each compound can be characterized by either of the general formulas:



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wherein each R^1 , R^2 , R^3 , R^4 , R^5 , Q^1 , Q^2 , X , a , b and c is as defined above.

In such a combinatorial array, typically each of the plurality of compounds has a different composition and each compound is at a selected region on a substrate such that each compound is isolated from the other compounds. This isolation can take many forms, typically depending on the substrate used. If a flat substrate is used, there may simply be sufficient space between regions so that there cannot be interdiffusion between compounds. As another example, the substrate can be a microtiter or similar plate having wells so that each compound is in a region separated from other compounds in other regions by a physical barrier.

The array typically comprises at least 10 ligands, compounds, complexes or compositions each having a different chemical formula, meaning that there must be at least one different atom or bond differentiating the plurality in the array. In other embodiments, there are at least 25 compounds, complexes or compositions on or in the substrate each having a different chemical formula. In still other embodiments, there are at least 50 or 96 or 124 ligands, compounds, complexes or compositions on or in the substrate each having a different chemical formula. Because of the manner of forming combinatorial arrays, it may be that each compound, complex or composition is not pure. Typically, each compound in the plurality of compounds is at least 50% pure within its region. In other embodiments, each element of the array comprises the composition of matter described above, comprising the ligand and a metal precursor. The same array discussion above applies to arrays of this type. In still other embodiments, each element of the array is a metal-ligand complex defined

above, including complexes V, VI, VII, VIII, IX, X, XI, XII, XIII, XIV, XV and XVI. The same array discussion above applies to arrays of this type.

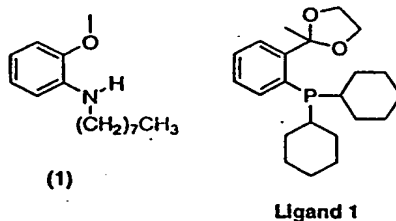
The catalytic performance (activity and/or selectivity) of the ligands of this invention in combination with a suitable metal precursor, compositions of this invention or metal-ligand complexes of this invention can be tested in a combinatorial or high throughput fashion. For any of the listed transformations, thin layer chromatography (TLC) in combination with imaging technology may be employed. TLC is well known in the art, see for example Vol. 1, *Thin-Layer Chromatography, Reagents & Detection Methods*, Jork et al. (VCH Publishers, New York, New York 1990), incorporated herein by reference. Polymerizations or oligomerizations can also be performed in a combinatorial fashion, see, e.g., commonly owned provisional U.S. Patent Application No. 60/096,603, filed August 13, 1998 (having attorney docket no. 65304-010), herein incorporated by reference. High throughput screening can also be performed optically and in parallel, for example, as disclosed in commonly owned U.S. Patent Applications 09/067,448, filed April 2, 1998, 08/947,085, filed October 8, 1997, and 08/946,135, filed October 7, 1997, each of which is incorporated by reference.

EXAMPLES

General: All reactions were performed under argon atmosphere in oven-dried glass Schlenk tubes using standard Schlenk techniques or in an inert atmosphere glove box. All aryl halides, all amines, sodium *t*-butoxide, bis(dibenzylideneacetone)palladium ($\text{Pd}(\text{dba})_2$), benzene, ethanol, diethyl ether, methylene chloride, toluene, and 1,4-dioxane were purchased from commercial sources and used as received. All solvents used were of the anhydrous, Sure-seal® grade. Column chromatography was performed using commercially available Silica Gel 60 (particle size: 0.063 – 0.100 mm), hexanes and ethyl acetate. GCMS analyses were conducted on a Hewlett-Packard 5890 instrument. ^1H , ^{13}C , ^{31}P NMR spectra were obtained using a Bruker 300 MHz FT-NMR spectrometer. Chemical shifts in ^1H and ^{13}C NMR spectra were calibrated with reference to the chemical shift of residual protiated solvent. Chemical shifts in ^{31}P NMR spectra were calibrated with reference to 85% H_3PO_4 ; a negative value of chemical shift denotes resonance upfield from H_3PO_4 .

EXAMPLE 1:

2-(Octylamino)anisole (1): A mixture of 2-chloro-anisole (0.12 mL, 0.94 mmol), octylamine (0.19 mL, 1.14 mmol), NaO^tBu (125 mg, 1.30 mmol), Pd(dba)₂ (12 mg, 0.02 mmol), Ligand 1 (22 mg, 0.06 mmol) in toluene (4 mL) at 105 °C for 3 hours and analyzed by GCMS. Ligand 1 was made in accord with the procedure disclosed in commonly assigned provisional U.S. patent application no. 60/095,612, filed August 8, 1998, incorporated herein by reference. The reaction was cooled to room temperature, taken up in diethyl ether (125 mL), washed with water (30 mL) and brine (30 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using hexanes as the eluent to afford the title compound, whose structure is shown below as compound (1), after drying under vacuum, as an colorless oil (yield: 230 mg, 95 %).

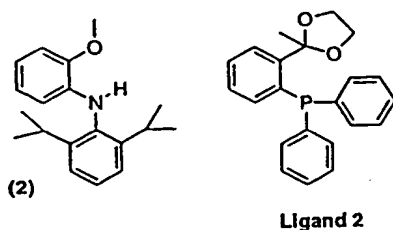


Analysis for the compound showed: ¹H NMR (CDCl₃): • 6.92 (t, J = 7.6 Hz, 1H, ArH), 6.81 (d, J = 7.6 Hz, 1H, ArH), 6.71 (d, J = 7.6 Hz, 1H, ArH), 6.67 (t, J = 7.6 Hz, 1H, ArH), 4.22 (br., 1H, -NH), 3.86 (s, 3H, -OCH₃), 3.16 (t, J = 7.2 Hz, 2H, -NCH₂-), 1.69 (pentet, 2H, -NCH₂CH₂CH₂-), 1.35 (br., 10H, 5 -CH₂-'s), 0.95 (br., 3H, CH₃). ¹³C NMR (CDCl₃): • 146.7, 138.5, 121.3, 115.9, 109.7, 109.3, 55.3, 43.7, 31.8, 29.5, 29.4, 29.2, 27.2, 22.6, 14.0.

EXAMPLE 2:

2-(2,6-Diisopropylanilino)anisole (2): The title compound, with the structure shown below, (439 mg, 97 % yield) was obtained as a colorless oil from the reaction of 2-bromoanisole (300 mg, 1.60 mmol), 2,6-diisopropylaniline (298 mg, 1.68 mmol), NaO^tBu (161 mg, 1.68 mmol), Pd(dba)₂ (18 mg, 0.03 mmol), Ligand 2 (30 mg, 0.08 mmol) in toluene (4 mL) at 105 °C for 1 hour. Work up for the compound was as in Example 1. Ligand 2 was made in accord with the procedure disclosed in commonly

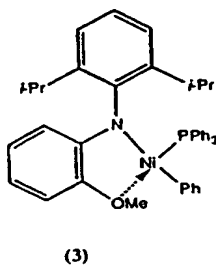
assigned U.S. patent application no. 09/062,128, filed April 17, 1998, herein incorporated by reference. Ligand 2 has the following structure:



Analysis for the title compound showed: ^1H NMR (CDCl_3): • 7.41 – 7.21 (m, 3 H, ArH), 6.94 (d, 1H, $J = 7.4$ Hz, ArH), 6.83 – 6.73 (m, 2H, ArH), 6.23 (d, 1H, $J = 7.4$ Hz, ArH), 5.72 (br., 1H, NH), 4.01 (s, 3H, OMe), 3.28 (heptet, 2H, $J = 6.9$ Hz, 2 CHMe_2 's), 1.25 (d, 12H, $J = 6.9$ Hz, 2 Me_2 's). ^{13}C NMR (CDCl_3): • 147.6, 146.2, 137.9, 135.4, 127.0, 123.7, 121.1, 116.7, 110.9, 109.7, 55.7, 28.1, 23.9. Anal. for $\text{C}_{19}\text{H}_{25}\text{NO}$; Calcd: C, 80.52; H, 8.89; N, 4.94; Found: C, 79.93; H, 8.89; N, 4.85.

EXAMPLE 3:

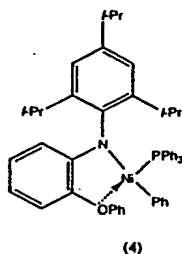
(2,6-(*i*-Pr) $_2$ C $_6$ H $_3$)N(2-MeOC $_6$ H $_4$))Ni(C $_6$ H $_5$)(PPh $_3$) (3): *trans*-Ni(PPh $_3$) $_2$ (Ph)(Cl) (241 mg, 0.35 mmol) was suspended in 5 mL Et $_2$ O and the suspension was cooled to -35°C . (2,6-(*i*-Pr) $_2$ C $_6$ H $_3$)(2-MeOC $_6$ H $_4$)NLi (102 mg, 0.36 mmol) was dissolved in 2 mL Et $_2$ O, the solution was cooled to -35°C and then added to the cooled suspension of *trans*-Ni(PPh $_3$) $_2$ (Ph)(Cl). The reaction was allowed to warm to room temperature and was stirred for 3 hours. A greenish-grey precipitate formed. The precipitate was collected, washed with Et $_2$ O (10 mL) and dried (yield = 148 mg; 60%). The complex has the following expected structure:



Analysis for the complex showed: ^1H NMR (C_6D_6): • 6.2–7.7 (m, 27H, Ar), 4.21 (sept, 2H, CHMe_2), 2.83 (s, 3H, OMe), 1.30 (overlapping doublets, 12H, CHMe_2)

EXAMPLE 4:

(2,4,6-(*i*-Pr)₃C₆H₂)N(2-PhOC₆H₄))Ni(C₆H₅)(PPh₃) (4): *trans*-
 Ni(PPh₃)₂(Ph)(Cl) (255 mg, 0.37 mmol) was suspended in 5 mL Et₂O and the
 5 suspension was cooled to -35°C. (2,4,6-(*i*-Pr)₃C₆H₂)(2-PhOC₆H₄)NLi (140 mg, 0.36
 mmol) was dissolved in 2 mL Et₂O, the solution was cooled to -35°C and then added
 to the cooled suspension of *trans*-Ni(PPh₃)₂(Ph)(Cl). The reaction was allowed to
 warm to room temperature and was stirred for 3 hours. Solvent was removed *in*
vacuo and the resulting red-brown solid was washed with hexane (10 mL) and dried
 10 (yield = 142 mg, 51%). The complex has the following expected structure:



Analysis for the complex showed: ¹H NMR (C₆D₆) • 6.0-7.2 (m, 31H, Ar), 4.25 (sept, 2H, *ortho*-CHMe₂), 2.91 (sept, 1H, *para*-CHMe₂), 1.42 (d, 6H, *para*-CHMe₂), 1.32 (overlapping doublets, 12H, *ortho*-CHMe₂).

EXAMPLE 5:

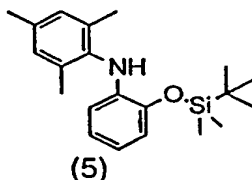
This example uses the complex of Example 3 with an activator to oligomerize ethylene. Complex (3) from Example 3 (24 mg, 0.035 mmol) and B(C₆F₅)₃ (40 mg, 0.078 mmol) were combined in a thick-walled glass flask fitted with a teflon valve.
 20 5.0 mL toluene was added and the mixture was stirred for 5 minutes. The mixture was placed under constant ethylene pressure (25 psi) and stirred for 1.5 hours. An aliquot of the reaction mixture was analyzed by ¹H NMR spectroscopy and the yield of oligomers was calculated by comparison of the integrals of the peaks associated with the ethylene oligomers to the integral of the toluene methyl peak (yield = 47
 25 mmol oligomers; 900 TO/hour).

EXAMPLE 6:

This example uses the complex of Example 4 with an activator to oligomerize ethylene. Complex (4) from Example 4 (27 mg, 0.035 mmol) and $B(C_6F_5)_3$ (70 mg, 0.136 mmol) were combined in a thick-walled glass flask fitted with a teflon valve. 5.0 mL toluene was added and the mixture was stirred for 5 minutes. The mixture was placed under ethylene (15 psi) and stirred for 15 minutes. An aliquot of the reaction mixture was analyzed by 1H NMR spectroscopy and the yield of oligomers was calculated by comparison of the integrals of the peaks associated with the ethylene oligomers to the integral of the toluene methyl peak (yield = 16.3 mmol oligomers; 1860 TO/hour).

EXAMPLE 7:

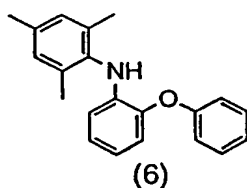
1-(*tert*-Butyldimethylsiloxy)-2-mesitylaminobenzene (5): The starting compound 1-bromo-2-(*tert*-butyldimethylsiloxy)benzene was first synthesized from the reaction of 2-bromophenol (9.58 g, 113 mmol) and *t*-butyldimethylsilylchloride (17.16 g, 114 mmol) in CH_2Cl_2 (about 100 mL) in the presence of imidazole (13.62 g, 200 mmol) at room temperature for 16 hours (yield 96%). See, T.W. Greene et al., *supra* for general details on this reaction. Subsequently, a mixture of 1-bromo-2-(*tert*-butyldimethylsiloxy)benzene (as synthesized above) (2.87g, 10.0 mmol), 2,4,6-trimethylaniline (1.35g, 10.0 mmol), sodium *tert*-butoxide (1.15g, 12.0 mmol), $Pd(dba)_2$ (29 mg, 50 μ mol) and Ligand 2 (shown above in Example 2) (35 mg, 100 μ mol) in 40 mL toluene was heated to 100 $^\circ C$ for 20 hr. The reaction was worked up by aqueous quenching and extraction with ether. The crude product was purified by flash chromatography on a silica gel column, affording 2.70 g of the desired material as a colorless oil (79 %). The compound (5) has the following structure:



Analysis for the compound showed: 1H -NMR ($CDCl_3$, 300 MHz) δ 0.26 (s, 6H), 1.02 (s, 9H), 2.14 (s, 6H), 2.29 (s, 3H), 5.45 (brs, 1H), 6.09 (dd, J = 1.5, 7.8, 1H), 6.56 (dt, J = 1.5, 7.7, 1H), 6.69 (dt, J = 1.5, 7.7, 1H), 6.77 (dd, J = 1.2, 7.5, 1H), 6.97 (s, 2H). MS (EI+) 341 (M+), 284 (bp).

EXAMPLE 8:

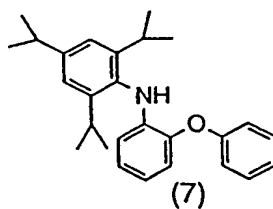
1-Mesitylamino-2-phenoxy-benzene (6): A mixture of 2-bromomesitylene (1.99g, 10.0 mmol), 2-phenoxyaniline (1.85g, 10.0 mmol), sodium *tert*-butoxide (1.15g, 12.0 mmol), Pd(dba)₂ (58 mg, 100 • mol) and Ligand 2 (shown above in Example 2) (70 mg, 200 • mol) in 50 mL toluene was heated to 100 °C for 6 days. The reaction was worked up by aqueous quenching and extraction with ether. The crude product was purified by flash chromatography on a silica gel column, affording 2.94 g of the desired material as a slightly yellow oil (97 %). The compound (6) has the following structure:



Analysis for the compound showed: ¹H-NMR (CDCl₃, 300 MHz) • 2.10 (s, 6H), 2.34 (s, 3H), 5.44 (brs, 1H), 6.22 (dd, *J* = 1.5, 8.0, 1H), 6.87-6.75 (m, 4H), 7.01-7.07 (m, 3H), 7.31 (t, *J* = 7.8, 2H). MS (EI+) 303 (M⁺).

EXAMPLE 9:

1-Phenoxy-2-(2,4,6-triisopropylphenoxy)benzene (7): A mixture of 2-bromo-1,3,5-triisopropylbenzene (2.83g, 10.0 mmol), 2-phenoxyaniline (1.85g, 10.0 mmol), sodium *tert*-butoxide (1.15g, 12.0 mmol), Pd(dba)₂ (58 mg, 100 • mol) and Ligand 2 (shown above in Example 2) (70 mg, 200 • mol) in 50 mL toluene was heated to 100 °C for 18 hr. The reaction was worked up by aqueous quenching and extraction with ether. The crude product was purified by flash chromatography on a silica gel column, affording 3.38 g of the desired material as a slightly yellow solid (87 %). The compound (7) has the following structure:



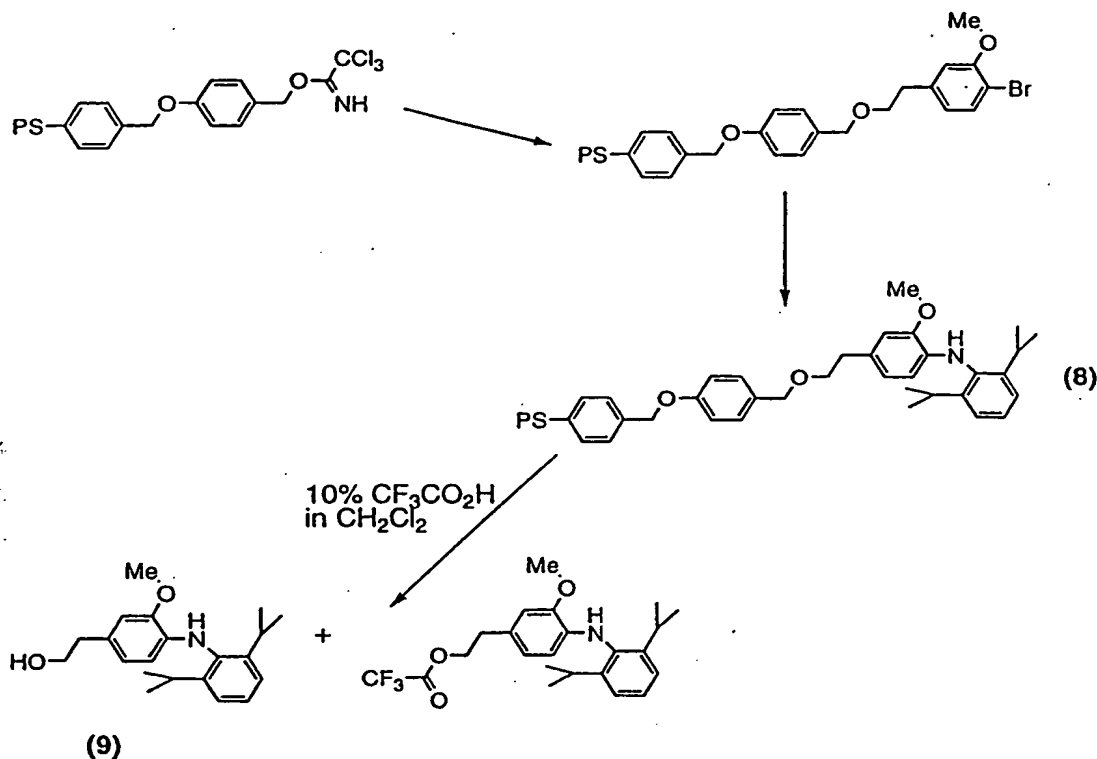
Analysis for the compound showed: $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) • 1.06 (d, $J = 6.8$, 12H), 1.25 (d, $J = 6.9$, 6H), 2.88 (sep, $J = 6.9$, 1H), 3.05 (sep, $J = 6.9$, 2H), 5.34 (brs, 1H), 6.24 (dd, $J = 1.3, 8.0$, 1H), 6.63 (dt, $J = 1.4, 7.8$, 1H), 6.89 (dt, $J = 1.1, 7.9$, 1H), 7.01-7.07 (m, 3H), 7.31 (dt, $J = 2.1, 8.6$, 2H). MS (EI+) 387 (M+).

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EXAMPLE 10:

This is an example of making a ligand on a solid support, in this case a resin bead having a tether. The tether, 2-(3-bromo-4-methoxyphenyl)ethanol, was first synthesized as follows: To 3-bromo-4-methoxyphenylacetic acid (12.26g, 50.0 mmol) in 100 mL tetrahydrofuran (THF) was added borane dimethylsulfide complex (6.0 mL, 60.0 mmol) with cooling in an ice bath. The reaction was stirred at room temperature overnight. The reaction mixture was concentrated in vacuo. The residue was taken up in 100 mL methanol and concentrated in vacuo to remove borate. This operation was repeated three times, affording analytically pure alcohol as a yellow oil (10.86 g, 94% yield). See N.M. Yoon, et al., *J. Org. Chem.*, **38**, 2786 (1973), herein incorporated by reference. Then, 2-(3-Bromo-4-methoxyphenyl)ethanol was immobilized onto Wang resin (100-200 mesh, 0.89 mmol/g loading) according to the procedure described by Hanessian and Xie (*Tetrahedron Letters*, **39**, 1998, 733-736), herein incorporated by reference. The resulting resin (1.50g, 1.14 mmol), 2,6-diisopropylaniline (404mg, 2.28 mmol), sodium *tert*-butoxide (219mg, 2.28 mmol), $\text{Pd}(\text{dba})_2$ (13 mg, 23 • mol) and Ligand 2 (shown above in Example 2) (16 mg, 46 • mol) in 10 mL toluene were heated to 100 °C for 23 hr. The resin was drained, washed with three times with 10mL of toluene (referred to as "10mLx3"), and then 10mLx5 THF, 10mLx3 DMF, 10mLx3 H₂O, 10mLx3 methanol, 10 mLx3 DMF, 10mLx3 THF, and 10mL CH₂Cl₂, and dried under vacuum, affording 1.61 g of tan color resin (100% based on the loading of the Wang resin). In order to characterize the resin, 144 mg of the resin was treated with 10 [v/v]% trifluoroacetic acid in CH₂Cl₂ for 30 min. at 21 °C. The resin was filtered off and rinsed with 1mL x5 CH₂Cl₂. The combined filtrates were washed with sat. aqueous NaHCO₃, dried over Na₂SO₄, filtered and concentrated, affording 24.9 mg of a brown oil. The GC-MS analysis of the cleaved product revealed a mixture of the desired coupling product (70%) and its trifluoroacetic acid ester (30%) that was presumably formed during the acid cleavage, and it did not show unreacted 2-(3-bromo-4-methoxyphenyl)ethanol. The resin bound ligand is shown below as structure

(8), and the cleaving reaction shows the unbound ligand as structure 9:

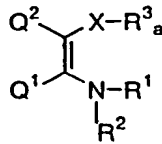


5 Analysis of the cleaved product (9) showed: ¹H-NMR (CDCl₃, 300 MHz) • 1.13 (d, J= 6.9, 6H), 2.61 (t, J= 6.6, 2H), 3.14 (sep, J= 6.6, 2H), 3.66 (t, J= 6.5, 2H), 3.94 (s, 3H), 5.62 (brs, 1H), 5.95 (d, J= 2.1, 1H), 6.51 (dd, J= 2.1, 8.1, 1H), 6.79 (d, J= 8.1, 1H), 6.89 (dt, J= 1.1, 7.9, 1H), 7.20-7.32 (m, 4H). MS (EI+) 327 (M+).

10 It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should, therefore, be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of
 15 equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated herein by reference for all purposes.

What is claimed is:

1. A compound characterized by the general formula:



- 5 wherein each R¹, R² and R³ is independently selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, R¹ and R² are joined together in a
10 ring structure;

- Q¹ and Q² are, independently, selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, Q¹ and Q² are joined together in a ring structure;

- X is selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus; and a is 1 or 2 depending on X.

2. The compound of claim 1, wherein each of R¹ and R² is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, heteroalkyl, cycloalkyl, substituted cycloalkyl, aryl and substituted aryl.

3. The compound of claim 1, wherein R¹ and R² are joined in a ring, wherein the said ring has between 5 and 10 non-hydrogen atoms.

- 25
4. The compound of claim 3, wherein said ring has between 5 and 6 non-hydrogen atoms in the backbone of the ring.

5. The compound of claim 1, wherein R¹ is a substituted or unsubstituted
30 phenyl.

6. The compound of claim 5, wherein R^1 is a substituted phenyl and there are from 1-5 substituents on said phenyl ring, with each of said substituents independently selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

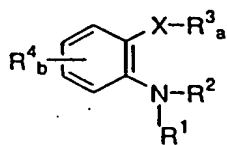
7. The compound of claim 6, wherein there are 1, 2 or 3 substituents on said substituted phenyl and said substituents are selected from the group consisting of chloro, fluoro, iodo, bromo, methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, phenyl, naphthyl, benzyl, trimethylsilyl and isomers thereof, where applicable.

8. The compound of claim 1, wherein X is oxygen, a is 1 and R^3 is selected from the group consisting of alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl and silyl.

9. The compound of claim 8, wherein R^3 is a substituted phenyl and there are from 1-5 substituents on said phenyl ring, with each of said substituents independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

10. The compound of claim 9, wherein there are 1, 2 or 3 substituents on said substituted phenyl and said substituents are selected from the group consisting of chloro, fluoro, iodo, bromo, methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, phenyl, naphthyl, benzyl, trimethylsilyl and isomers thereof where applicable.

11. The compound of claim 1, wherein Q^1 and Q^2 are joined together in a ring structure with the backbone of the compound, such that the compound can be characterized by the general formula:



wherein R^1 , R^2 , R^3 , X and a each have the definition given above; R^4 is selected from the group consisting of electron withdrawing and electron donating groups; and b is 0, 1, 2, 3 or 4.

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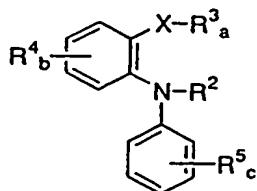
12. The compound of claim 11, wherein R^4 is selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, silyl, amino, alkoxy, aryloxy, phosphino, boryl, transition
10 metals, halogens and combinations thereof.

13. The compound of claim 12, wherein b is 1, 2 or 3 and R^4 is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, phenyl, cyano, acetyl, benzoyl, nitro, dimethylamino, diethylamino, methylphenylamino,
15 benzylmethylamino, trimethylsilyl, dimethylboryl, diphenylboryl, methylphenylboryl, dimethoxyboryl, chromium tricarbonyl, ruthenium tricarbonyl, cyclopentadienyl iron and isomers thereof where applicable.

14. The compound of claim 11, wherein two or more R^4 groups combine to
20 form a fused ring structure with the aromatic group that forms a part of the ligand backbone.

15. The compound of claim 14, wherein the aromatic group that is part of the backbone as combined with two or more R^4 groups that have formed a fused ring are
25 substituted or unsubstituted naphthalene, substituted or unsubstituted quinoline or substituted or unsubstituted indole.

16. The compound of claim 11, wherein R^1 is a substituted or unsubstituted phenyl such that the compound can be characterized by the general formula:



wherein R^2 , R^3 , R^4 , X , a and b each have the definition given above, R^5 is selected from the group consisting of electron withdrawing and electron donating groups; and c is 0, 1, 2, 3, 4 or 5.

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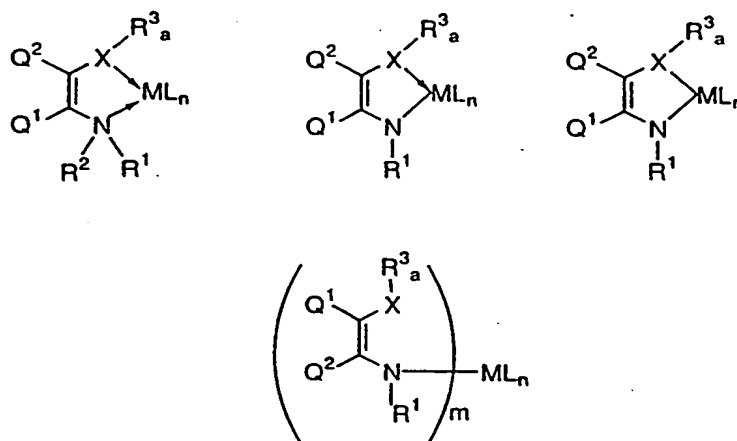
17. The compound of claims 16, wherein R^5 is selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, silyl, amino, alkoxy, aryloxy, phosphino, boryl, transition
10 metals, halogens and combinations thereof.

18. The compound of claim 17, wherein there are two R^5 groups that are joined in a fused ring structure with the phenyl ring.

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19. The compound of claim 18, wherein there are four R^5 groups that are joined in a fused ring structure with the phenyl ring.

20. A complex characterized by one of the following general formulas:



5 wherein each R^1 , R^2 and R^3 is independently selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, R^1 and R^2 are joined together in a
10 ring structure;

Q^1 and Q^2 are, independently, selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations
15 thereof; optionally, Q^1 and Q^2 are joined together in a ring structure;

X is selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus; a is 0, 1 or 2 depending on X and the type of bonding to M ;

M is a transition metal selected from the group consisting of Groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table of Elements;

20 L is independently each occurrence, a ligand;

n is a number 0, 1, 2, 3, 4, and 5; and

m is 1, 2, 3 or 4.

21. The complex of claim 20, wherein M is selected from the group consisting
25 of Sc, Y, Zr, Ti, Hf, V, Nb, Ta, Zn, Mo, Mn, W, Fe, Ru, Os, Co, Rh, Ni, and Pd.

22. The complex of claim 21, wherein M is selected from the group consisting of Pd, Ni, Co, Fe, Ru, Rh, Cr, Mo, Mn, and V.

5 23. The complex of claim 20, wherein L is selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, cyclopentadienyl, substituted cyclopentadienyl, imido, oxo and
10 combinations thereof.

24. The complex of claim 20, wherein L is selected from the group consisting of alkene, diene, carbon monoxide, isocyanide, nitrous oxide, PA_3 , NA_3 , OA_2 , SA_2 , SeA_2 , and combinations thereof, wherein each A is independently selected from a
15 group consisting of alkyl, substituted alkyl, heteroalkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, and amino.

25. The complex of claim 20, wherein R^1 is a substituted or unsubstituted
20 phenyl.

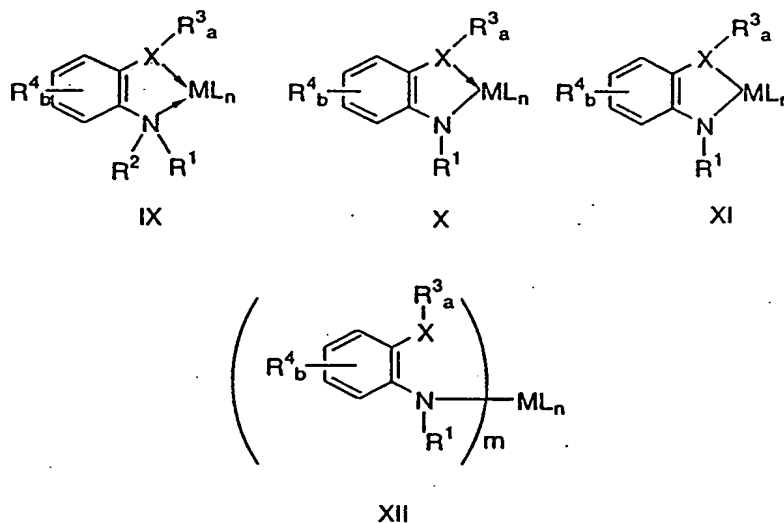
26. The complex of claim 25, wherein R^1 is a substituted phenyl and there are from 1-5 substituents on said phenyl ring, with each of said substituents independently selected from the group consisting of halogens, alkyl, substituted alkyl,
25 cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

27. The complex of claim 26, wherein there are 1, 2 or 3 substituents on said
30 substituted phenyl and said substituents are selected from the group consisting of chloro, fluoro, iodo, bromo, methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, cyclooctyl, phenyl, naphthyl, benzyl, trimethylsilyl and isomers thereof.

28. The complex of claim 20, wherein X is oxygen, a is 1 and R³ is selected from the group consisting of alkyl, substituted alkyl, aryl, substituted aryl or silyl.

29. The complex of claim 28, wherein R³ is a substituted phenyl and there are
5 from 1-5 substituents on said phenyl ring, with each of said substituents independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

30. The complex of claim 20, wherein Q^1 and Q^2 are joined together in a ring structure with the backbone of the compound, such that the compound can be characterized by one of the following general formulas:



wherein R^1 , R^2 , R^3 , X , M , L , n , m and a each have the definition given above; R^4 is selected from the group consisting of electron withdrawing and electron donating groups; and b is 0, 1, 2, 3 or 4.

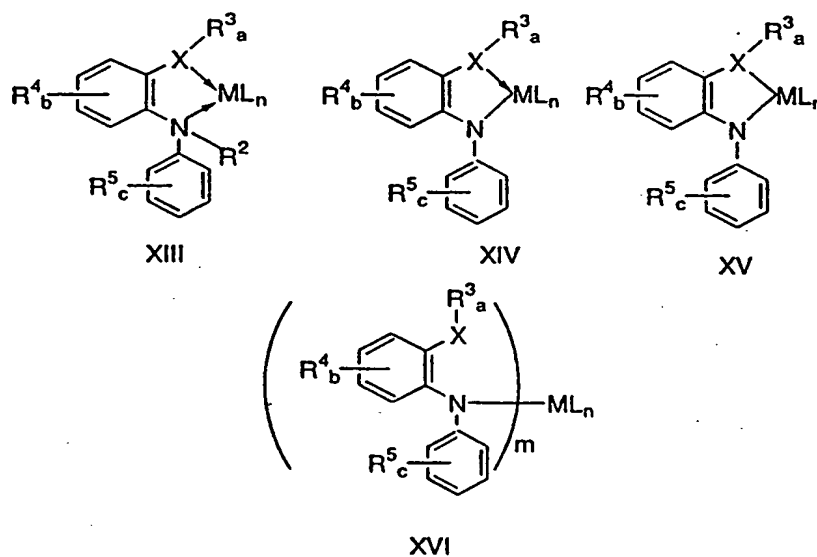
31. The complex of claim 30, wherein R^4 is selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, silyl, amino, alkoxy, aryloxy, phosphino, boryl, transition metals, halogens and combinations thereof.

32. The complex of claim 31, wherein b is 1, 2 or 3 and R^4 is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, phenyl, cyano, acetyl, benzoyl, nitro, dimethylamino, diethylamino, methylphenylamino, benzylmethylamino, trimethylsilyl, dimethylboryl, diphenylboryl, methylphenylboryl, dimethoxyboryl, chromium tricarbonyl, ruthenium tricarbonyl, cyclopentadienyl iron and isomers thereof where applicable.

33. The complex of claim 32, wherein two or more R^4 groups combine to form a fused ring structure with the aromatic group that forms a part of the ligand backbone.

34. The complex of claim 33, wherein the aromatic group that is part of the backbone as combined with two or more R^4 groups that have formed a fused ring are substituted or unsubstituted naphthalene, substituted or unsubstituted quinoline or substituted or unsubstituted indole.

35. The complex of claim 30, wherein R^1 is a substituted or unsubstituted phenyl such that the compound can be characterized by one of the following general formulas:



wherein R^2 , R^3 , R^4 , X , M , L , n , m , a and b each have the definition given above, R^5 is selected from the group consisting of electron withdrawing and electron donating groups; and c is 0, 1, 2, 3, 4 or 5.

36. The complex of claim 35, wherein R^5 is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, silyl, amino, alkoxy, aryloxy, phosphino, boryl, transition metals, halogens and combinations thereof.

37. A composition of matter comprising the compound of claim 1 and a metal precursor characterized by the general formula $M(L)_n$, where M is a transition metal selected from the group consisting of Groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table of Elements; L is independently each occurrence, a ligand; and n is a number 0, 1, 2, 3, 4, and 5.

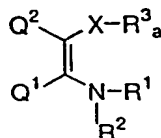
38. The composition of claim 37 wherein the ratio of compound to metal precursor is in the range of about 0.01:1 to about 100:1.

39. The composition of claim 38, wherein the ratio of compound to metal precursor is in the range of about 0.5:1 to about 20:1.

40. The composition of claim 37, wherein the compound is of claim 11.

41. The composition of claim 37, wherein the compound is of claim 16.

42. An array comprising a plurality of compounds wherein each compound can be characterized by the general formula:



wherein each R^1 , R^2 and R^3 is independently selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, R^1 and R^2 are joined together in a ring structure;

Q^1 and Q^2 are, independently, selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl,

alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, Q¹ and Q² are joined together in a ring structure;

X is selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus; and a is 1 or 2 depending on X.

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43. The array of claim 42, wherein each of said plurality of compounds has a different composition.

44. The array of claim 42, wherein each of said plurality of compounds is at a
10 selected region on a substrate such that each compound is isolated from the other compounds.

45. The array of claim 42, wherein said plurality of compounds comprises at least 10 compounds each having a different composition.

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46. The array of claim 45, wherein said plurality of compounds comprises at least 25 compounds each having a different composition.

47. The array of claim 46, wherein said plurality of compounds comprises at
20 least 50 compounds each having a different composition.

48. The array of claim 44, wherein said substrate is a microtiter plate.

49. The array of claim 44, wherein said plurality of compounds are at least
25 50% pure within said regions.

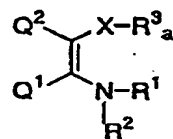
50. A transition metal-catalyzed reaction employing complex in claim 20.

51. The reaction of claim 50, wherein the reaction involves C-H, C-C, C-N, C-
30 O, C-S, C-P, C-B and C-Si bond formation.

52. The reaction of claim 51, wherein C-H, C-C, C-N, C-O, C-S, C-P, C-B, and C-Si bond formation involves a sp²-hybridized C atom.

53. The reaction of claim 52, wherein the reactions involve carbonylation, hydroformylation, hydroxycarbonylation, hydrocarbonylation, hydroesterification, hydrogenation, hydrosilylation, hydroboration, hydroamination, epoxidation, aziridination, reductive amination, C-H activation, insertion, C-H activation-insertion, C-H activation-substitution, C-halogen activation, C-halogen activation-substitution, C-halogen activation-insertion, alkene metathesis, alkyne metathesis, polymerization, alkene oligomerization, alkene polymerization, alkyne oligomerization, alkyne polymerization, co-polymerization, CO-alkene co-oligomerization, CO-alkene co-polymerization, CO-alkyne co-oligomerization, and CO-alkyne co-polymerization.

54. A polymerization or oligomerization reaction employing a compound characterized by the general formula:



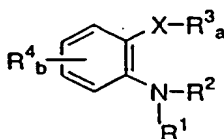
wherein each R^1 , R^2 and R^3 is independently selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, R^1 and R^2 are joined together in a ring structure;

Q^1 and Q^2 are, independently, selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, Q^1 and Q^2 are joined together in a ring structure;

X is selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus; and a is 1 or 2 depending on X .

55. The reaction of claim 54, wherein each of R^1 and R^2 is independently selected from the group consisting of alkyl, substituted alkyl, heteroalkyl, cycloalkyl, substituted cycloalkyl, aryl and substituted aryl.

56. The reaction of claim 54, wherein Q^1 and Q^2 are joined together in a ring structure with the backbone of the compound, such that the compound can be characterized by the general formula:



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wherein R^1 , R^2 , R^3 , X and a each have the definition given above; R^4 is selected from the group consisting of electron withdrawing and electron donating groups; and b is 0, 1, 2, 3 or 4.

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57. The reaction of claim 56, wherein R^4 is selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, silyl, amino, alkoxy, aryloxy, phosphino, boryl, transition metals, halogens and combinations thereof.

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58. The reaction of claim 57, wherein b is 1, 2 or 3 and R^4 is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, phenyl, cyano, acetyl, benzoyl, nitro, dimethylamino, diethylamino, methylphenylamino, benzylmethylamino, trimethylsilyl, dimethylboryl, diphenylboryl, methylphenylboryl, dimethoxyboryl, chromium tricarbonyl, ruthenium tricarbonyl, cyclopentadienyl iron and isomers thereof where applicable.

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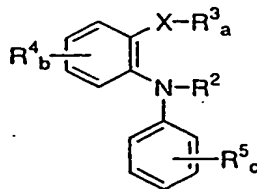
59. The reaction of claim 56, wherein two or more R^4 groups combine to form a fused ring structure with the aromatic group that forms a part of the ligand backbone.

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60. The reaction of claim 59, wherein the aromatic group that is part of the backbone as combined with two or more R^4 groups that have formed a fused ring are substituted or unsubstituted naphthalene, substituted or unsubstituted quinoline or substituted or unsubstituted indole.

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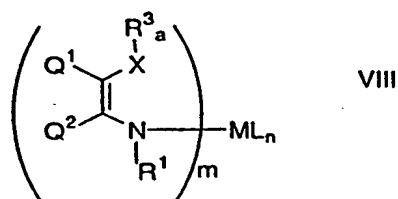
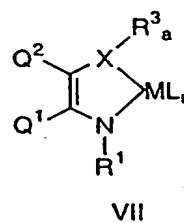
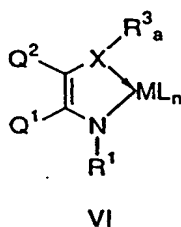
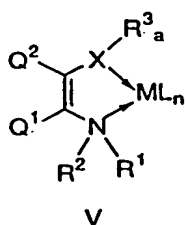
61. The reaction of claim 56, wherein R^1 is a substituted or unsubstituted phenyl such that the compound can be characterized by the general formula:



- 5 wherein R^2 , R^3 , R^4 , X, a and b each have the definition given above, R^5 is selected from the group consisting of electron withdrawing and electron donating groups; and c is 0, 1, 2, 3, 4 or 5.

62. The reaction of claims 61, wherein R^5 is selected from the group
 10 consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, silyl, amino, alkoxy, aryloxy, phosphino, boryl, transition metals, halogens and combinations thereof.

63. A process for polymerizing or oligomerizing an olefin, diolefin or acetylenically unsaturated compound, comprising contacting said olefin, diolefin or acetylenically unsaturated compound to a complex that can be characterized by one of the following general formulas:



- wherein each R^1 , R^2 and R^3 is independently selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, R^1 and R^2 are joined together in a ring structure;

- Q^1 and Q^2 are, independently, selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, Q^1 and Q^2 are joined together in a ring structure;

- X is selected from the group consisting of oxygen, nitrogen and phosphorus; a is 0, 1 or 2 depending on X and the type of bonding to M ;

M is a transition metal selected from the group consisting of Groups 4, 5, 6, 7, 8, 9 and 10 of the Periodic Table of Elements;

L is independently each occurrence, a ligand;

n is a number 0, 1, 2, 3, 4, and 5; and

m is 1, 2, 3 or 4.

64. The process of claim 63, further including an activator.

5 65. The process of claim 63, further comprising the step of subjecting the complex to an activating technique.

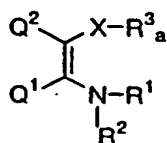
66. The process of claim 63, wherein M is selected from the group consisting of Sc, Y, Zr, Ti, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ni and Pd.
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67. The process of claim 63, wherein L is selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino,
15 thio, seleno, cyclopentadienyl, substituted cyclopentadienyl, imido, oxo and combinations thereof.

68. The process of claim 63, wherein L is selected from the group consisting of carbon monoxide, isocyanide, nitrous oxide, PA_3 , NA_3 , OA_2 , SA_2 , SeA_2 , and
20 combinations thereof, wherein each A is independently selected from a group consisting of alkyl, substituted alkyl, heteroalkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, and amino.

25 69. The process of claim 63, wherein said process is a continuous process at a temperature of between -100°C and 500°C .

70. A process for making a compound characterized by the general formula:
formula:



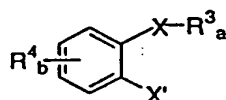
wherein each R^1 , R^2 and R^3 is independently selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, R^1 and R^2 are joined together in a ring structure;

Q^1 and Q^2 are, independently, selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, Q^1 and Q^2 are joined together in a ring structure;

X is selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus; and a is 1 or 2 depending on X ;

the step of the process comprising:

reacting a compound characterized by the general formula:



where X' is selected from the group consisting of chloro, bromo, iodo, triflate, nonaflate, alkyl sulfonates, aryl sulfonates and tosylate;

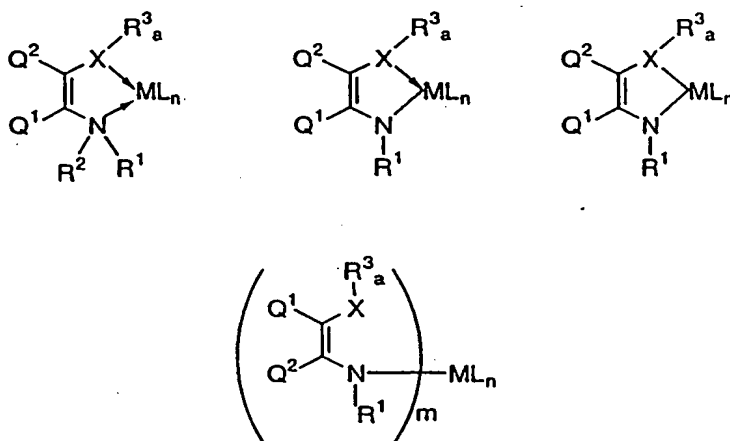
with an amine characterized by the general formula HNR^1R^2 , where R^1 and R^2 are as defined above.

71. The process of claim 70, wherein the step employs a catalyst that is a composition comprising M' and L' where M' is a homogeneous or heterogeneous metal precursor catalyst or catalyst and L' is a phosphine or nitrogen containing ligand.

72. The process of claim 71, wherein L' is ligand that is either bidentate, tridentate or hemi-labile and is unsubstituted or substituted, supported or unsupported, water-soluble or insoluble, soluble or insoluble in organic solvents.

5 73. The process of claim 71, wherein M' includes a metal selected from the group consisting of Pd, Ni or Pt.

74. An array comprising a plurality of complexes wherein each complex can be characterized by one of the following general formulas:



wherein each R¹, R² and R³ is independently selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, R¹ and R² are joined together in a ring structure;

Q¹ and Q² are, independently, selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally, Q¹ and Q² are joined together in a ring structure;

X is selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus; a is 0, 1 or 2 depending on X and the type of bonding to M;

M is a transition metal selected from the group consisting of Groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table of Elements;

L is independently each occurrence, a ligand;

n is a number 0, 1, 2, 3, 4, and 5; and

5 m is 1, 2, 3 or 4.

INTERNATIONAL SEARCH REPORT

Intern. nat. Application No.

PCT/US 99/23255

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C217/84 C07C217/92 C07F7/18 C07F15/04 C08F4/80

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SADIGHI J P ET AL: "A Highly Active Palladium Catalyst System for the Arylation of Anilines" TETRAHEDRON LETTERS, NL, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, vol. 39, no. 30, 23 July 1998 (1998-07-23), pages 5327-5330, XP004123224 ISSN: 0040-4039 page 5329; table 1	1,2,5-8, 11,12, 16,17, 70-73
X	DE 11 19 297 B (FARBENFABRIKEN BAYER AG) 1961 examples example 15	1,2,5,8, 11,12,16
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

22 February 2000

Date of mailing of the international search report

15/03/2000

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Pauwels, G

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/23255

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 34961 A (IMUTA JUNICHI ;SAITO JUNJI (JP); FUJITA TERUNORI (JP); SUGIMURA KE) 13 August 1998 (1998-08-13)	1-73
X	-& EP 0 893 454 A page 32 -page 36 examples 4,32 claims	
X	J.I.G. CADOGAN ET AL.: "Reduction of nitro-and nitroso-compounds by tervalent Phosphorus reagents. Part XII. Conversion of Aryl 2-nitroaryl ethers into novel 3-aryl-2,3-dihydro-1,3,2-benzoxaphosph(v)oles (oxaphosphoranes) and their 2-oxo-derivatives" JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 1,1975, pages 2376-2385, XP000876946 LETCHEWORTH GB page 2381, right-hand column, last paragraph page 2383, right-hand column, paragraph 1 page 2383, right-hand column, last paragraph page 2384, right-hand column, last paragraph page 2385, right-hand column, line 3	1,2,5-8, 11,12, 16,17
X	J.P. WOLFE ET AL.: "An improved catalyst system for aromatic carbon-nitrogen bond formation: the possible " JOURNAL OF THE AMERICAN CHEMICAL SOCIETY., vol. 118, 1996, pages 7215-7216, XP002131108 DC US page 7216: Scheme 1, compound 4 page 7216; table 1	1,2,5,8, 11,16, 17, 20-25, 28,30, 31, 35-41, 50-52, 70-73
X	BHARUCHA K R ET AL: "P-Alkoxyanilines as antinitrosamine agents for bacon" J. AGRIC. FOOD CHEM. (JAFCAU,00218561);1986; VOL.34 (5); PP.814-18, XP002131109 Canada Packers Inc.;Toronto; M6N 1K4; ON; Can. (CA) page 815; table I page 816; table IV	1,2,8, 11,12
	-/-	

INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/US 99/23255

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WARD Y D ET AL: "Solid phase synthesis of aryl amines via palladium catalyzed amination of resin-bound aromatic bromides" TETRAHEDRON LETT. (TELEAY, 00404039); 1996; VOL. 37 (39); PP. 6993-6996, XP002131110 Boehringer Ingelheim Pharmaceuticals Inc.; Dep. Chem. Development; Ridgefield; 06877; CT; USA (US) page 6994 -page 6995; tables 1, 2	1, 2, 5, 8, 11, 12, 16, 42-49, 70-73
X	R.J. SUNDBERG ET AL. : "Acid-promoted aromatic substitution processes in photochemical and thermal decompositions of aryl azides" JOURNAL OF ORGANIC CHEMISTRY, vol. 38, no. 11, 1973, pages 2052-2057, XP000876948 EASTON US example 1G; table I	1, 2, 5, 8, 11, 12, 16
X	A.I. PROKOF'EV ET AL: "Tautomerism and stereodynamics of indophenols, amidines, and their derivatives and analogs, IV. Paramagnetic complexes" RUSSIAN JOURNAL OF GENERAL CHEMISTRY., vol. 59, 1989, pages 1264-1272, XP002131159 CONSULTANTS BUREAU., US ISSN: 1070-3632 page 1267 page 1268 page 1269	1, 2, 5-13, 16, 17, 20-41

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/23255

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 50-53
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/SA/ 210

Continuation of Box I.2

Claims Nos.: 50-53

Present claims relate to an extremely large number of possible compounds, products or methods. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds, products or methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds, products or methods involving those compounds etc. prepared in the examples and closely related homologous compounds i.e. compounds of claim 1 in which Q1 and Q2 are joined and form a homo monocyclic aromatic ring, R1 is hydrogen, R2 phenyl, substituted in 2 and 6 position by 1-4 saturated alkyl and optionally substituted in position 4 by 1-4 saturated alkyl, X is oxygen, R3 is alkyl, phenyl or trialkylsilyl or R3 is linear saturated alkyl with more than 5 carbon atoms.

Present claims 50 to 53 relate to an extremely large number of possible methods. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the method of claim 54.

Documents known to the International Searching Authority relating to non-searched subject matter have been cited.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 99/23255

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 1119297 B		CH 392550 A DE 1119295 B FR 1284523 A NL 104211 C US 2008335 A US 2898335 A	04-07-1962 16-07-1935 04-08-1959
WO 9834961 A	13-08-1998	CA 2251471 A CN 1220672 T EP 0893454 A	13-08-1998 23-06-1999 27-01-1999